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## THEORETICAL CHEMISTRY INSTITUTE

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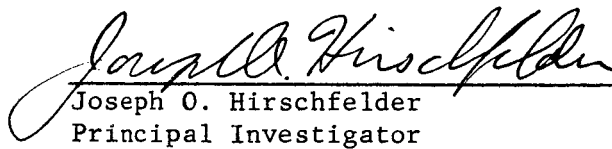
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Joseph O. Hirschfelder
Principal Investigator

# NASA SEMI-ANNUAL PROGRESS REPORT

## INTRODUCTION

Everybody seems to be working hard and we have some excellent research cooking, as evidenced by the technical parts of this report.

On October 4 - 6, with the joint sponsorship of the Mathematics Research Center, U. S. Army, we held a symposium on perturbation theory based upon our mathematical needs.  This symposium was unique in bringing together top mathematicians to learn about problems of physicists and chemists.  The physicists and chemists in turn learned about new mathematical techniques which will help them in their work.  The program for this symposium is attached to this report as Appendix A.  The technical papers which were presented will be published as a monograph by John Wiley and Sons.

We are very happy to watch the new chemistry building take shape.  In May 1967 we are looking forward to moving into new quarters which will consist of the eighth floor together with a portion of the ninth floor.

Val Pratt has joined the staff of the Theoretical Chemistry Institute as the director of our computer group.  One of his responsibilities is to set up a computer satellite in our new quarters which will join up with the large computer in the University of Wisconsin Computing Center.

We want to thank NASA once more for providing us with an excellent research opportunity.  We hope that we will be able to live up to the trust which you have placed in us.

## RESEARCH INTERESTS OF THE THEORETICAL CHEMISTRY INSTITUTE STAFF

There is a wide range of research at the Theoretical Chemistry Institute. W. Byers Brown, Saul T. Epstein, J. O. Hirschfelder, and Arnold C. Wahl are currently working on molecular and intermolecular quantum mechanics problems. Frank C. Andrews and C. F. Curtiss are concerned with the theory of statistical mechanics and transport properties. Richard B. Bernstein, C. F. Curtiss, and William A. Lester, Jr. are interested in molecular beams and scattering theory. Stuart E. Lovell is interested in scattering theory. John E. Harriman is working on electron-spin resonance and quantum mechanical density matrices. The following is a summary of the detailed research interests of each of the staff members.

<u>FRANK C. ANDREWS</u>

Current research activities are on the equilibrium and non-equilibrium statistical mechanics of dense classical gases and on non-equilibrium thermodynamics. The equilibrium statistical mechanics is an investigation of properties in the dense gas and liquid regions based on an observation that the chemical potential may be viewed very simply and intuitively for a system in the limit of large volume and number of particles. These investigations are shedding light on the validity of the van der Waals equation, on the liquid-vapor phase transition, and on how to view experimental data on the equilibrium properties of fluids. Since this entire approach is new, it is too early to say for sure what will come out of it. We have achieved a simple, intuitive formulation of the results of Uhlenbeck, Kac, and Hemmer[1] on the validity of the one-dimensional van der Waals equation. This led to work demonstrating the coexistence of condensed and dilute phases in one-dimensional classical fluids[2] and to a theoretical study of droplet formation in one-dimensional fluids.[3]

In non-equilibrium statistical mechanics, the formulation of a functional equation for reduced, several-particle distribution functions and the formulation of a generalized Boltzmann equation for the one-particle distribution function have been obtained from the reduced Liouville (BBGKY) equation in the form of a density expansion.[4] The stress in this work is on understanding the physical implications of the results and on mathematical simplicity. It is felt, for example, that the range of validity of Bogoliubov's hypothesis[5] that $f_s$ rapidly becomes a functional of $f_1$ is now understood in terms of the initial information available about the system.

There is continued interest in basic problems of irreversibility in mechanics.[6] A paper is in preparation[7] examining what the theoretician

can say about the Onsager reciprocal relations from a macroscopic point of view. Another paper is in preparation formulating transport coefficients in the form of time correlation functions based on some very general arguments, getting around the usual fluctuation-dissipation theorem.

An area in which work is being undertaken is that of the statistical mechanical theory of dielectric relaxation in liquids. Such a basic question as "What are the necessary and sufficient conditions for the validity of the Debye equations?" is yet to be answered. This work is being done in conjunction with Professor Worth E. Vaughan of the Chemistry Department.

There is interest in a number of problems in the statistical mechanical theory of the mechanical properties of polymer solutions.

There is also a continuing interest in certain more or less pedagogical problems in both classical and non-equilibrium thermodynamics.

The long-term goals of this research are increased physical and theoretical understanding of the structure of liquids and dense gases, both at equilibrium and out of equilibrium, and of the liquid-vapor phase transition.

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[1] M. Kac, G. E. Uhlenbeck, and P. C. Hemmer, J. Math. Phys. 4, 216 (1963).

[2] F. C. Andrews and J. M. Benson, Physics Letters, in press.

[3] F. C. Andrews, Physics Letters, in press.

[4] F. C. Andrews, J. Math. Phys. 6, 1496 (1965).

[5] N. N. Bogoliubov, "Problems of a Dynamical Theory in Statistical Physics," 1946, English translation in Studies in Statistical Mechanics, vol. 1. North-Holland Publishing Co., Amsterdam, 1962.

[6] F. C. Andrews, Proc. Natl. Acad. Sci. U. S. 53, 1284 (1965); 54, 13 (1965).

[7] F. C. Andrews, given at the December meeting of the American Institute of Chemical Engineers in Philadelphia.

### RICHARD B. BERNSTEIN

The research of R. B. Bernstein and associates which receives NASA support deals primarily with the problems of atom-atom elastic scattering and rotational excitation of diatomic molecules upon atomic collision.

The work on elastic scattering has been concerned with those special features of the behavior of the cross sections which are most sensitive to the interaction potential, especially to the attractive well. The recent research on the extrema-effect and its relation to the intermolecular potential well (carried out in collaboration with Mr. T. J. O'Brien) has been presented at the Discussion of the Faraday Society on "Intermolecular Forces" in Bristol, England, September, 1965.

In collaboration with Dr. C. F. Curtiss, Mr. H. T. Wood (now Dr.) and Mr. S. Imam-Rahajoe, a detailed study is near completion dealing with the quasi-bound states associated with the existence of three turning points, quantum mechanical tunneling through the centrifugal barrier, the resonances and their influence upon low energy scattering behavior.

An offshoot of this study has been a separate investigation of the relationship between the pattern of (predicted) resonances in elastic atom-atom scattering and the predissociation spectra of the composite diatomic molecule.

A computational study of proton-helium scattering at low energies, with the collaboration of G. G. Weber (formerly research associate) and Mrs. N. H. Gordon, has been completed. As an outgrowth of the work, using similar techniques, a parallel investigation of the scattering of metastable by ground state helium atoms (and a number of other systems) is being initiated in collaboration with Dr. W. A. Lester, Jr.

The research on the sudden approximation applied to the calculation of rotational excitation and scattering of polar diatomic molecules by atoms, in collaboration with Dr. K. H. Kramer (formerly research associate), is still in progress. A conceptual difficulty regarding the evaluation of the so-called "action integrals" has been resolved, and a definitive set of tables of these integrals has been prepared. New computations on collisional rotational transition probabilities ($j,m \rightarrow j',m'$) and inelastic cross sections using these action integrals are in progress, with the help of Mr. R. W. Fenstermaker.

The work on the more rigorous time-independent (S-matrix) method of treating the rotational excitation problem as applied to homonuclear diatomics is being continued by Dr. W. A. Lester, Jr. The computational problem of solving the many coupled differential equations efficiently is being attacked with some success. It is hoped to examine the solutions in the borderline region of total angular momentum where the distorted-wave approximation breaks down. The results for simple "model" interaction potentials will be compared with those obtained via the sudden approximation. Eventually one should be able to deal with real systems, at least those for which an estimate of the (anisotropic) interaction potential can be made.

The goal of the entire rotational excitation research program is a practical method of prediction of differential and total cross sections for rotational energy transfer.

# W. BYERS BROWN

The fundamental technical problems in the molecular quantum mechanics of stationary states are (a) electron repulsion, and (b) the many-center Coulomb field in molecules. Most of my current research is concerned with applying perturbation theory to these problems. Thus, I.D and II.B are concerned with problem (a), while II.A and III.C are concerned with (b).

The following summary of my research activities, together with my collaborators, is divided into three parts:

I. Work reported in June 1965 and now essentially completed.

II. Work reported in June 1965 and continuing.

III. New research projects, planned or underway.

## I. Work essentially completed

A). Perturbation Theory of Force Constants. (In collaboration with Dr. Margaret Lowe Benston).

This work is in the final computational stage.

B). Perturbation Theory of the Constrained Variational Method. (In collaboration with Dr. Delano P. Chong).

The application of the method developed by the author (J. Chem. Phys. 43, 0000 (1 January 1965)) to accurate calculations on LiH by Browne and Matsen (1964) is essentially complete and will be reported shortly.

The computational aspects of this problem have been explored further by Chong and Rasiel (WIS-TCI-119).

C). Perturbation Investigation of Delta Model for Diatomic Molecules. (In collaboration with Miss Pearl S. C. Wang).

This work has been brought to a successful conclusion and tends to support the application of perturbation theory by T. Y. Chang and the author (WIS-TCI-114) to CO based on $N_2$. The results are reported in

WIS-TCI-130 (December 1965) and will be published shortly.

D). <u>Perturbation Treatment of $H_2$ Based on $H_2^+$.</u> (In collaboration with Mr. Robert L. Matcha).

This research is reported in Dr. Matcha's Ph.D. thesis, reproduced as WIS-TCI-129. It completely vindicates the application of perturbation theory to electron repulsion in a simple diatomic molecule from the point of view of accuracy.

E). <u>Cusp Conditions for Molecular Wave Functions.</u> (In collaboration with Mr. Russell T. Pack and Dr. J. O. Hirschfelder).

The research reported in WIS-TCI-123 has been developed slightly further, and will be submitted for publication soon.

II. <u>Work continuing</u>

A). <u>Perturbation Expansion of Molecules Based on the United Atom.</u> (In collaboration with Mr. James D. Power).

This problem concerns the expansion of the electronic energy W in powers of the internuclear distances. Four aspects are being attacked:

(1) The unproven assumption made by the author in the derivation of the formula for $W_3$ for diatomics in WIS-TCI-105.

(2) The alternative expansion of W for diatomics in powers of $Z_a Z_b / Z^2$ .

(3) The form of $W_3$ for polyatomic molecules (this is intimately connected with 3-centre integrals).

(4) The form of $W_4$ for diatomics. This coefficient has two parts, one involving $(Z_a Z_b / Z^2)$, which is known, and the other involving $(Z_a Z_b / Z^2)^2$, which is unknown, and is the first really interesting term in the expansion of W.

Mr. Power is calculating values of $W_2$, $W_3$ and the known part of $W_4$ for 2-6 electron atoms for various values of Z and states of interest.

B). <u>First-order Perturbation Equation for Helium: Hooke's Law Model</u>. (In collaboration with Mr. Ronald J. White).

The basic donkey work on the exact solution, and Hartree-Fock approximation, for the model is reported in WIS-TCI-116 (29 August 1965), and will be published shortly.

Present research is directed towards the analysis of partial differential equations for the Legendre components $F_\ell(r_1, r_2)$ of the first-order wave functions $\psi^{(1)} = \psi^{(0)} F(r_1, r_2, \cos \theta_{12})$ . The function F is known for the model but not for the actual helium atom. Mr. White has discovered, by using a technique introduced by C. Schwartz (1963), that the functions $F_\ell$ for the actual helium atom and the model are asymptotically the same for large $\ell$ .

C). <u>Thomas-Fermi Model for Diatomic Molecules</u>. (In collaboration with Mr. Robert E. Roberts and Dr. S. T. Epstein).

Computations giving an upperbound to the energy for a wide range of internuclear distance and any atomic number for neutral homonuclear molecules have been completed. Similar computations on a lower bound are being carried out. Also the absence of van der Waals dispersion attraction for this model is being investigated.

III. <u>New work</u>

A). <u>Use of Group Theory to Simplify Calculations of Eigenvalues and Eigenvectors</u>.

An inconvenience associated with the use of group theory to factorize secular equations occurring in quantum mechanics is that particular realizations of degenerate irreducible matrix representations $\Gamma$ appear

to be required. This is a curious situation, since the eigenvalues and eigenvectors are independent of any particular realization. The author showed some years ago (unpublished work) that it is possible to express the irreducible factors of the secular determinant in an explicitly invariant form involving only the group characters. This work was resuscitated as a result of a visit to the Institute by Professor P. O. Löwdin, and is being extended in the light of recent developments.

B). <u>Short Range Interaction Between Atoms.</u> (In collaboration with Dr. Rodger B. Hake).

Conventional calculations of the repulsion energy between two atoms become awkward for distances less than about 0.5A. On the other hand, the united atom expansion only works well for much shorter distances, say 0.0-0.1A. The short range, less than 0.5A, has recently begun to be explored experimentally by Everhart and others, and there is now considerable interest in theoretical potentials in this range.

The possibility of developing a theory suitable for this range is being investigated on the basis of the following ideas:

(1) treat electron repulsion as a perturbation;

(2) use elliptic coordinates $\xi, \eta, \phi$ and work with the $Y_{\ell m}(\eta, \phi)$ components of the wave function;

(3) utilize the beautiful and simple mathematical results of MacRobert (1948) and Livingston (1965) for the Euler transforms which occur.

C). <u>Long Range Interactions Between Atoms.</u> (In collaboration with Miss Pearl S. C. Wang).

In a recent paper by Ovchinnikov and Sukhanov (1965) the asymptotic exponential (overlap) terms in the electronic energy of $H_2^+$ have been

obtained. This work is being extended to a heteronuclear one-electron diatomic molecule to discover the dependence of the various long-range terms on the atomic numbers $Z_a$ and $Z_b$.

D). <u>Quadrupole-Quadrupole Interaction Constants for Atoms</u>. (In collaboration with Mr. Tai Yup Chang).

The long-range interaction of atoms in states other than S-states is frequently dominated by the first-order quadrupole-quadrupole interaction, which leads to an interaction energy $-C_5/R^5$. The theory of the constant $C_5$ has been thoroughly worked out by Knipp (1938), but the expectation values of $r^2$ involved do not appear to have been recalculated with accurate wave functions.

Dr. Bernstein at the Institute has recently discovered a way of obtaining long-range atomic interaction constants $C_n$ from the predissociation spectra of diatomic molecules. It is therefore proposed to calculate $C_5$ for an extensive set of atoms and states by two methods: (1) from the atomic Hartree-Fock wave functions of Clementi, (2) by using screening constants obtained by Dalgarno's technique of setting first-order corrections equal to zero.

## C. F. CURTISS

We have continued our study of the theory of transport phenomena in gases. In particular, we have continued the study of quantum effects, the effects of internal degrees of freedom, and density effects on the values of the transport coefficients. During this period, four Ph.D. theses based on these studies were completed.

In previous studies, we had developed expansions of the transport cross-sections as series in powers of Planck's constant. Explicit expressions were obtained for the classical term and the first four quantum corrections. These correction terms were evaluated numerically for a realistic potential function, the Lennard-Jones potential, using the CDC 1604 computer. These results form a portion of the Ph.D. thesis of Herbert T. Wood. In previous work we had evaluated the quantum mechanical transport cross-sections through the evaluation of the phase shifts by direct solution of the Schroedinger equation. This direct method is useful in the low temperature region where the corrections are large. In an intermediate temperature range in which the corrections are small, but significant, the direct evaluation is too lengthy even for a large computer. The series development provides information in this intermediate temperature range. The series development is, however, only asymptotically convergent. Numerically it appears that the region in which the series is useful is not sufficiently large to overlap with the region in which the earlier direct results were obtained. David Bennett is developing a modification of the series development, which it is hoped will have a larger range of convergence. In this way we hope to obtain numerical results over the entire range of the variables. The primary significance of this development is that it

may confirm (or possibly conflict with) earlier results which we have obtained concerning the limit as h→ 0 of the quantum expressions for the cross sections.

We have also continued our study of the effects of internal degrees of freedom on the transport coefficients. We have obtained explicit expressions for the quantum mechanical differential cross sections for collisions between loaded spheres in which the load is just slightly off center. These results were then used to obtain expressions for the transport properties of such a gas. This probably represents the first exact quantum mechanical evaluation of the transport coefficients of a gas of molecules with internal degrees of freedom. We have shown that the classical limits of the quantum expressions are identical with the results previously obtained from a direct classical development by Dahler. This development forms the Ph.D. thesis of John J. Mueller.

In connection with our study of the effects of internal degrees of freedom on the transport coefficients we have also continued our study of the inelastic and elastic collisions between atoms and ions. As a prototype of more complex processes, we considered in detail collisions between a proton and a hydrogen atom. In his Ph.D. thesis, Donald J. Kouri considered the formal theory of this scattering process making full use of the symmetries of the Hamiltonian. In particular, the invariance of the Hamiltonian to a rotation of the entire system permits the separation of three rotational coordinates from the Schroedinger equation. In a similar manner, the identity of the protons leads to further simplifications, which are of importance in connection with the implications of the Pauli principle.

We are also continuing our study of density effects on the transport coefficients. In a previous study, expressions and numerical values of the viscosity and thermal conductivity second virial coefficients were obtained by Hoffman. The numerical results obtained by Hoffman, using the Lennard-Jones potential, agree reasonably well with the experimental values at high temperatures. At low temperatures considerable disagreement occurs. This disagreement is very probably due to the effect of bound states which were not considered properly in the theoretical development. This difficulty was introduced by an approximation which plays an essential role in the development. This approximation involves the mechanism by which bound pairs of molecules are formed and destroyed. The approximation has, we presume, little effect on the results at high temperatures but is poor at low temperatures. R. Soesanto Imam-Rahajoe is continuing our study of this problem. In this study we are retaining the basic approximation introduced by Hoffman but considering the parallel quantum mechanical development. The physical idea behind this approach is that due to tunneling the classical bound states of positive energy are not bound in a quantum treatment. It is expected that this will eliminate most of the error in the classical treatment of the problem.

Finally, we concluded our development of a statistical mechanical derivation of the magnetohydrodynamic equations of change. This development is the Ph.D. thesis of Raymond Beshinske.

## SAUL T. EPSTEIN

### Research Activities

1). Continued interest in trying to determine an optimal "Unperturbed Hamiltonian" to go with a given "Unperturbed Wave Function".

2). An accurate value for the magnetic susceptibility of $He^+$ should soon be available (Matcha and Lyon). This will then be compared with what the theories of Hameka and of Pople would predict. This will test the **further approximation** these authors make **beyond** the one-electron approximation itself.

3). We have studied various connections between calculations of the van der Waal's potential between two atoms which use conventional second order perturbation theory, and calculations which are based on the frequency dependent polarizabilities of the isolated atoms.

4). In connection with the problem of long range forces between atoms we are investigating ways of treating the Pauli Principle as a perturbation.

5). We plan to produce the "Sturmian Functions" (see M. Rotenberg, Annals of Phys. 19, 262 (1962)) for $H_2^+$ and then investigate their usefulness as a basis set for molecular calculations.

6). We plan a numerical investigation of the Thomas-Fermi model for a diatomic molecule (with Byers Brown and R. Roberts) in order to see in detail the origins of Teller's theorem (Rev. Mod. Phys. 34, 627 (1962)) that there is no molecular binding.

7). Calculations are progressing on the ground state of Beryllium (with J. Karl) using $r_{ij}$ terms in the wave functions.

8). Calculations are progressing on the Lamb Shift in $H_2$ (with J. D. Garcia).

JOHN E. HARRIMAN

The goal of our research program is a better understanding of the electronic structure of molecules, particularly those with open shells as in free radicals, and of magnetic energy levels in molecular systems. Emphasis is placed on aspects which can be investigated by electron spin resonance.

I. A Comparison and Extension of Molecular SCF Methods. (In collaboration with Ken Sando, Lloyd Holm, and Dr. Arturo Hardisson).

Molecular self-consistent field calculations can be done in a variety of ways for open shell systems such as free radicals and triplet states. The conventional or restricted method involves a closed shell of doubly occupied orbitals and an open shell in which all electrons have the same spin. In the unrestricted method the closed shell orbitals are split to give different orbitals for different spins. The resulting function can be made an eigenfunction of $S^2$ by application of a projection operator. If the function is in the form of a spin-projected single determinant but the orbitals are chosen to minimize the energy after projection then the result is frequently called extended SCF.

The most commonly used criterion for how "good" a wave function is, the energy associated with it, can be applied to these various SCF methods. We are making a general comparative investigation. When will the unrestricted SCF energy be lower than the restricted; when will the energy be decreased by spin projection; and how do extended SCF energies compare with these others? We have general energy expressions for the various methods, and we expect to compare also the results of specific calculations.

It is well known that other properties, such as the spin density distribution, are more affected by projection than is the energy. We are

investigating various molecular unrestricted SCF wave functions and the effect of projection on spin properties. A perturbation treatment of "spin-polarization" effects commonly encountered in electron spin resonance spectroscopy is also getting under way.

Although the wave function corresponding to a spin-projected single determinant is known in the general case, this general form is not convenient for use in calculations. Expressions have been known for several years which give the first order reduced density matrix for the projected state conveniently in terms of that for the unprojected state. We are now in the process of obtaining similar expressions for the second order density matrix. We hope to apply them to such problems as the calculation, in the projected-unrestricted SCF approximation, of zero-field splittings in molecular triplets and of the spin-other orbit contribution to a g-factor anisotropy in free radicals.

We have had available for some time the theoretical basis for extended SCF calculations by a density matrix method. Unfortunately, computational problems not directly associated with the critical features of the problem have thus far prevented effective test of the method. Work in this area is continuing.

Some of this work will be reported at the international colloquium on "Magnetic Hyperfine Structure of Atoms and Molecules" in Paris, June 1966.

II. Molecular Magnetic Energy Levels and Time Dependent Effects in Electron Spin Resonance.

Interest in these areas continues. At present, however, our major effort here has been directed toward the establishment of experimental

facts. Experimental work receives support from sources other than NASA.

III. Quantum Mechanical Density Matrices.

Work continues on density matrix theory. In addition to the density matrices associated with SCF theory, we are investigating density matrices of more complex functions. The n-representability problem, and relationships among density matrix components are being investigated in certain special cases.

JOSEPH O. HIRSCHFELDER

I. Magnetic and Relativistic Intermolecular Forces

A). Moderately Large Separations (10A to 200A), [ in collaboration with Hojing Kim and W. J. Meath ] . We are making a systematic study of various types of intermolecular forces which are due to magnetic and relativistic effects. One paper (by Meath and Hirschfelder) has been accepted for publication in the J. Chem. Phys. Recently Kim has treated the energy of interaction between two hydrogen atoms in their ground states. He is currently working on the interaction of one hydrogen atom in its ground state, the other in a 2s or 2p state where resonance make the calculations much more difficult but the results much more interesting.

B). Very Long Range Retardation Interactions (separations greater than 200A), [ in collaboration with Duane Condiff and W. J. Meath ] . At very large separations relativistic retardation effects change the nature of intermolecular forces. One paper on this subject (by Meath and Hirschfelder) has already been accepted for publication by the J. Chem. Phys. Condiff is finding that he can reproduce the Casimir and Polder results for the interaction of two molecules in their ground states by using reaction field techniques together with classical electrodynamic considerations, instead of using quantum field theory and summing twenty-seven Feynman diagrams. The long range interaction of one molecule in an electronically excited state with a molecule in its ground state is very interesting since the energy of interaction varies as $R^{-2}$. If the molecules are the same species, the energy varies as $R^{-1}$. Thus, an electronically excited molecule will interact strongly with a surface which may be as much as $10^{-4}$ cm distant. We are trying to design an experiment to measure this behavior. This effect may be of considerable interest in biological

systems, catalysis, etc. We shall explore these possibilities.

II.  A Calculation of Intermolecular Forces Using Perturbation Techniques,
[in collaboration with W. A. Sanders and W. D. Lyon ] .  We are trying to
apply perturbation techniques to intermolecular force problems at small
separations were the charge distributions overlap.  Our efforts up to the
present time have not been satisfactory (although we will get a journal
publication).  However, we are currently working on a very promising
approach which concentrates on the expectation value of the coordinates of
two electrons.  For example, we are trying to get good values of $\langle x_1 x_2 \rangle$ .
If the two electrons are in the same atom, good values of this expectation
value ensure good values of the polarizability.  If the two electrons are
on different atoms, this type of correlation ensures good intermolecular
forces.

III.  A New Method for Calculating Bipolar Angle Averages and Two-Center,
Two-Particle Integrals Involving $r_{12}$,  [in collaboration with Milleur and
Twerdochlib ] .  A remarkably simple procedure is found for calculating
bipolar angle averages of a two-center, two-particle function.  Our pro-
cedure is based upon simple geometrical considerations.  This bipolar angle
average can be used as a first step in calculating two-center, two-particle
integrals involving $r_{12}$.  The bipolar angle average and the bipolar angle
average weight functions which are tabulated may be useful for the deter-
mination of radial distribution functions or to assist in the analysis of
x-ray crystallography or electron defraction.

IV.  Molecular Orbitals,  [in collaboration with A. C. Wahl ] .  It is
found that Slater screening constants can be used to estimate the size of
some molecular orbitals, others are too distorted by polarization and
electron transfers to bear much resemblance to the separated atom orbitals.

V.  <u>Chemical Reaction Rate Theory</u>,  [in collaboration with Duane Condiff, Michael Stern and Carol Sanna ] .  The relative rates of isotopic chemical reactions depend upon the reflection and transmission coefficients of wave packets moving on a potential energy surface.  We idealize these potential energy surfaces by two-dimensional wave guides such that we can solve the resulting two-dimensional quantum mechanical problems exactly.  We are currently working on two types of problems:

A)  Two straight troughs which meet at an angle.

B)  A straight trough joining a circular segment which joins a second straight trough.

In the circular segment we are calculating a very interesting type of Bessel function, $\Phi_n$ (r) .  Here $\Phi_n$ = 0 at the two boundaries of our wave guide, $r = r_0$ and $r = r_0 + a$ .  In between, $\Phi_n$ has (n-1) modes. The $\Phi_n$ are linear combinations of Bessel functions of the first and second kinds.  For small values of n , the order of the Bessel functions are real; but for large values of n , the order is pure imaginary.

Professor Rudolph Marcus at the University of Illinois is making similar calculations on similar potential energy surfaces using classical (instead of quantum) mechanics to calculate the transmission and reflection coefficients.  We shall probably publish our results jointly.

VI.  <u>Molecular Models Displayed by Computers</u>,  [in collaboration with Carol Constable ] .  We have developed a computing machine program for displaying a space filling molecular model of the Hirschfelder-Fisher type as viewed from an arbitrary direction.  Our input is the set of coordinates of each of the atoms together with their species.  This work is being supported by the National Institutes of Health.  We are looking forward to coupling these displays with the solutions of dynamical equations in order to show moving pictures of the normal modes of molecules.  We have reason

to believe that the normal modes of enzymes and other biological molecules may be quite surprising.

### STUART E. LOVELL

The work on high energy atom-ion collisions described in the previous report continues. This work has been carried out in collaboration with Dr. M. B. McElroy of the Kitt Peak National Observatory. Basically, the approach used is to expand the wave function for the colliding system in linear combinations of atomic wave functions centered on the two centers. Making certain approximations appropriate for high energies and massive particles, one obtains a set of simultaneous, first order, differential equations. The number of equations equals the number of atomic wave functions used in the expansion.

We have paid particular attention to the effect on the calculated cross sections of including a varying number of atomic states in the expansion. Our aim here is not the calculated values per se., but to obtain a qualitative and semi-quantitative understanding of the simpler models to aid in understanding more complicated systems for which calculations are not feasible. A second report on this work is now in progress.

The solution of the differential equations describing the system is a formidable computation even when a restricted number of atomic states are used. If only two states, one on each center are used, and if the system is symmetric, e.g., proton-hydrogen, then one may obtain the solution in integral form.

In the so-called Born formulation of the problem one obtains an integral equation representation of the solution. Exact solution of this integral equation is possible only if one knows the true, time dependent wave function for the system, which, of course, one does not. A systematic sequence of approximate solutions (not necessarily convergent) for the Born equation are ordinarily used. We suggest here an alternate approximation.

It is simply to use in place of the true wave function the above mentioned two state solution.

In so far as we know this is a new approximate solution to the Born equation. It is admittedly usable only for symmetric systems and probably only at high (i.e., greater than 5Kev) energies. However it is computationally feasible and, we expect, of satisfactory accuracy.

## ARNOLD C. WAHL

I. Development of analysis and general multiconfiguration-multicenter program
for the CDC 3600 with first planned usage being ab initio studies of simple
chemical reactions. Program is being written in fortran and in a modular
fashion more easily transcribable to the next generation of computers.

II. Extended-Hartree-Fock studies of diatomic molecules with emphasis on
the proper description of molecular formation and dissociation. Calculations
on $H_2$, $Li_2$ and $F_2$ have been completed which indicate that only a few of what
we call Optimized-Valence-Configurations are necessary to give reasonable
binding energies and spectroscopic constants. The NaK molecule is being
studied in detail by this method.

III. **Pictorial Studies of Molecules.** Automatic charge density contour
hunting and plotting programs have been developed for the CDC 3600 which we
are using to visually study gross features of chemical binding, ionization
in molecules, and electron correlation as achieved by added optimal-
configurations.

IV. Hartree-Fock Studies of $He_2$, $He_2^+$, $F_2^-$, $Ne_2^+$, $Ne_2$, $Cl_2$, $Cl_2^-$, $Ar_2^+$, $Ar_2$,
with the goal of illucidating chemical binding and interatomic forces in
terms of localized orbitals and various types of contributions to the total
energy. All of the above systems with the exception of $Cl_2$ dissociate
properly in the Hartree-Fock approximation and thus are reasonable candidates
for this study. Although primarily motivated by its interpretative aspect
this study yields wave function and properties useful in themselves.

V. The analysis and technology of calculating molecular properties from
computed wave functions is being extensively developed. Our goal being the
reliable prediction of binding energies, spectroscopic constants, multipole
moments, field gradients, magnetic susceptibility, ionization potentials,
and transition probabilities.

# SUMMARY OF EXPENDITURES AND UNLIQUIDATED COMMITMENTS

Theoretical Chemistry Institute portion of NASA Grant NsG-275-62

July 1, 1965 - December 31, 1965

| | Expenditures | Unliquidated Commitments | Totals |
|---|---|---|---|
| Salaries | $100,408.00 | $20,464.70 | $120,872.70 |
| Computing Services | 31,547.94 | 4,977.11 | 36,525.05 |
| Travel | 1,534.93 | | 1,534.93 |
| Publications | 647.34 | 3,924.40 | 4,571.74 |
| Services | 408.99 | 35.32 | 444.31 |
| Supplies | 2,043.83 | 366.67 | 2,410.50 |
| Communications | 595.37 | 1,795.85 | 2,391.22 |
| Honoraria for Consulting Services | 3,445.40 | 2,077.50 | 5,522.90 |
| Total Direct Costs | $140,631.80 | $33,641.55 | $174,273.35 |
| Overhead* | 28,126.36 | 6,728.31 | 34,854.67 |
| Computing Equipment** | 61,000.00 | | 61,000.00 |
| Total Costs | $229,758.16 | $40,369.86 | $270,128.02 |

\*   20% of Total Direct Costs

\*\*  Surplus from fiscal year 1964-65 research budget

APPENDIX A

Attached is the program from the Invitational Advance Seminar on Perturbation Theory and Its Application in Quantum Mechanics, October 4 - 6, 1965, which was sponsored jointly by the Theoretical Chemistry Institute and the Mathematics Research Center, U. S. Army, at the University of Wisconsin.

APPENDIX B - <u>Theoretical Chemistry Institute Short-Term Visitors</u>

<u>During the Period 1 July 1965 through 31 December 1965</u>

| <u>NAME AND ADDRESS</u> | <u>PERIOD OF VISIT</u> | <u>LECTURES GIVEN</u> |
|---|---|---|
| Dr. Abraham Ben-Reuven<br>National Bureau of Standards<br>Washington, D. C. | 7/1 - 31/65 | Liouville Spaces, Pressure<br>  Broadening & Microwave<br>  Spectra<br>Pressure Shifts of Vibra-<br>  tion-Rotation Spectra of<br>  Linear Molecules |
| Dr. Philip Rosen<br>Hasbrouck Physics Laboratory<br>University of Massachusetts<br>Amherst, Massachusetts | 7/1 - 8/31/65 | Dispersion Relation for<br>  a Longitudinal Plasma<br>  Wave in the Presence<br>  of a Magnetic Field |
| Dr. Peter D.Robinson<br>Department of Mathematics<br>University of York<br>York, England | 7/1 - 9/30/65 | |
| Dr. Robert Yaris<br>Department of Chemistry<br>University of Washington<br>St. Louis, Missouri | 7/1 - 15/65 | |
| Professor Rudolph A. Marcus<br>Depts. of Chemistry & Chemical<br>  Engineering<br>University of Illinois<br>Urbana, Illinois | 7/6 - 8/5/65 | Electron Transfer Reactions<br>  in Solution & at Electrodes<br>Generalization of Activated<br>  Complex Theory<br>Analytical Mechanics &<br>  Chemical Kinetics |
| Dr. Milton Lietzke<br>Oak Ridge National Laboratory<br>Oak Ridge, Tennessee | 7/9/65 | |
| Dr. Morton Eliason<br>Department of Chemistry<br>Augustana College<br>Rock Island, Illinois | 7/9/65 | |
| Professor Howard S. Taylor<br>Department of Chemistry<br>University of So. California<br>Los Angeles, California | 7/12 - 16/65 | Quantum Chemistry &<br>  Resonant Scattering<br>  Theory |

| NAME AND ADDRESS | PERIOD OF VISIT | LECTURES GIVEN |
|---|---|---|
| Prof. Peter R. Fontana<br>Department of Physics<br>University of Michigan<br>Ann Arbor, Michigan | 8/1 - 6/65 | |
| Prof. Edwin A. Power<br>Department of Mathematics<br>University College<br>Longon, England | 9/22/65 | Long Range van der Waals<br>and Resonance Forces |
| Prof. Inga Fischer-Hjalmars<br>Inst. for Theoretical Physics<br>University of Stockholm<br>Stockholm, Sweden | 9/26 - 30/65 | Semiempirical Parameters<br>in MO Theory |
| Prof. Alec Dalgarno<br>Department of Applied Mathematics<br>The Queen's Univ. of Belfast<br>Belfast, North Ireland | 10/4 - 8/65 | Further Applications of<br>Perturbation Theory |
| Prof. Per-Olov Löwdin<br>Quantum Chemistry Group<br>University of Uppsala<br>Uppsala, Sweden | 10/4 - 8/65 | Aronszajn Projections in<br>the Theory of Lower<br>Bounds |
| Dr. Howard Reiss, Director<br>North American Aviation Science<br>  Center<br>Thousand Oaks, California | 10/18 - 19/65 | |
| Dr. Frank Moran<br>North American Aviation Science<br>  Center<br>Thousand Oaks, California | 10/18 - 19/65 | |
| Dr. J. A. Barker<br>Division of Physical Chemistry<br>Commonwealth Scientific &<br>  Industrial Organization<br>Australia | 11/4 - 5/65 | Intermolecular Forces<br>in Argon |
| Prof. Geoffrey Gee<br>Northwood Research Center<br>Midland, Michigan | 11/15/65 | |

APPENDIX C - <u>University of Wisconsin Theoretical Chemistry Institute</u>

<u>Staff - July 1, 1965 through December 31, 1965</u>

| <u>NAME</u> | <u>TITLE</u> |
|---|---|

<u>Research Staff</u>:

| | |
|---|---|
| Joseph O. Hirschfelder | Professor of Chemistry; Director, Theoretical Chemistry Institute |
| Charles F. Curtiss | Professor of Chemistry; Associate Director, Theoretical Chemistry Institute |
| Richard B. Bernstein | Professor of Chemistry |
| William Byers Brown | Professor of Chemistry |
| Saul T. Epstein | Professor of Physics |
| Frank C. Andrews | Assistant Professor of Chemistry |
| Arnold C. Arthurs | Visiting Assistant Professor of Theoretical Chemistry |
| John E. Harriman | Assistant Professor of Chemistry |
| Stuart E. Lovell | Assistant Professor of Computer Sciences |
| Arnold C. Wahl | Assistant Professor of Chemistry |
| William A. Lester, Jr. | Assistant Director, Theoretical Chemistry Institute |

<u>Post-Doctorate Staff</u>:

| | |
|---|---|
| Margaret L. Benston<br>University of Washington<br>Ph.D. 1964 | Project Associate |
| Duane W. Condiff<br>University of Minnesota<br>Ph.D. 1965 | NSF Post-Doctoral Fellow |
| John L. Graves<br>University of Chicago<br>Ph.D. 1956 | Project Associate |
| Rodger B. Hake<br>University of Leicester<br>Ph.D. 1965 | Project Associate |

Post-Doctorate Staff (cont'd)

| NAME | TITLE |
|---|---|
| Arturo Hardisson<br>University of London<br>Ph.D. 1962 | Project Associate |
| Earle R. Kebbekus<br>Pennsylvania State University<br>Ph.D. 1965 | Research Associate |
| Hojing Kim<br>Johns Hopkins University<br>Ph.D. 1965 | Project Associate |
| Robert J. Silbey<br>University of Chicago<br>Ph.D. 1965 | NAS-NRC Post-Doctorate Fellow |

Computing Staff:

| | |
|---|---|
| Marilyn L. Beuchel | Student |
| Carol E. Constable | Project Assistant |
| Wanda W. Giese | Project Assistant |
| Nahida H. Gordon | Project Assistant |
| Diane L. Hanson | Project Assistant |
| Marilyn A. Howard | Project Assistant |
| Linda E. Hulbert | Project Assistant |
| Carol M. Sanna | Project Assistant |

Graduate Students:

| | |
|---|---|
| David E. Bennett | Research Assistant |
| Peter J. Bertoncini | Research Assistant |
| Robert J. Beuhler | Research Assistant |
| Tai Yup Chang | Research Assistant |
| Jerry Drennan | Teaching Assistant |
| Roger W. Fenstermaker | Teaching Assistant |

Graduate Students (Cont'd)

| NAME | TITLE |
|------|-------|
| Jose D. Garcia | Research Assistant |
| Lloyd M. Holm | Research Assistant |
| R. Soesanto Imam-Rahajoe | Fellow, Agency for International Development |
| John H. Karl | Research Assistant |
| William D. Lyon | Research Assistant |
| Robert L. Matcha | Research Assistant |
| Mac Brown Milleur | Research Assistant |
| John J. Mueller | Research Assistant |
| Thomas J. O'Brien | Research Assistant |
| Russell T. Pack | NSF Fellow |
| James D. Power | Research Assistant |
| Robert E. Roberts | NASA Fellow |
| Kenneth M. Sando | Teaching Assistant/Research Assistant |
| Michael Twerdochlib | Research Assistant |
| Theodore G. Waech | Research Assistant |
| Thomas C. Wallace | Teaching Assistant |
| Pearl S. C. Wang | Research Assistant |
| Ronald J. White | NASA Fellow |

Office Staff:

| | |
|------|-------|
| Karen A. Rick | Project Assistant |
| Gloria M. Lawton | Stenographer III |
| Linda M. Becker | Stenographer II |
| Mary A. Wilson | Typist III |
| Marjorie J. Heil | Typist II |

APPENDIX D - <u>Summary of Research at the Theoretical Chemistry Institute</u>

<u>During the Period July 1, 1965 through December 31, 1965</u>

SUDDEN APPROXIMATION APPLIED TO ROTATIONAL EXCITATION OF MOLECULES BY ATOMS.
II.  SCATTERING OF POLAR DIATOMICS by R. B. Bernstein and K. H. Kramer
(supported by NASA and APL).

Report No. WIS-TCI-91                                     dated 13 July 1965

Will be submitted for publication to J. Chem. Phys.

### ABSTRACT

The sudden approximation is applied to the computation of rotational
transition probabilities and inelastic total cross sections for the scat-
tering of polar and non-polar diatomic molecules (rigid rotors) by atoms.
The calculations are based upon an interaction potential which includes
both short- and long-range anisotropies.  At thermal energies the long-
range attractive parts of the potential are of principal importance in
determining the inelasticity, with the main contribution arising from the
quadrupole interaction term (varying as $R^{-7} \cos^3 \theta$ ) .  The computations
show the rapid onset of "dominant-coupling" behavior (randomization of
transition probability among all close-coupled states) for impact parameters
below about $(S/\pi)^{\frac{1}{2}}$, where $S$ is the total inelastic total cross section.

SUDDEN APPROXIMATION APPLIED TO ROTATIONAL EXCITATION OF MOLECULES BY ATOMS.
II.  SCATTERING OF POLAR DIATOMICS by R. B. Bernstein and K. H. Kramer
(supported by NASA and APL).

Report No. WIS-TCI-91 (Erratum)                     dated 24 September 1965

Will be submitted for publication to J. Chem. Phys. along with WIS-TCI-91.

A STATISTICAL DERIVATION OF THE HYDRODYNAMIC EQUATIONS OF CHANGE FOR A
SYSTEM OF IONIZED MOLECULES by Raymond J. Beshinske (supported by NASA and
NSF).

Report No. WIS-TCI-110                                 dated 5 August 1965

Will not be published in this form.

## ABSTRACT

Non-relativistic, classical statistical mechanics is used to describe a dense fluid of molecules composed of nuclei and electrons with a purely coulomb interaction potential. A general equation of change is derived for the time rate of change of any macroscopic (ensemble averaged) dynamical variable. From this general equation, Maxwell's equations in a medium and the hydrodynamic equations of change are derived and expressed in terms of molecular properties, e.g. polarization and magnetization densities. These equations are discussed in the limiting case of low density and compared with previous results.

THE QUANTUM CORRECTIONS TO THE TRANSPORT COLLISION INTEGRALS by Herbert T. Wood (supported by NASA).

Report No. WIS-TCI-111                                    dated 10 August 1965

Will not be published in this form.

## ABSTRACT

The second quantum correction to the phase shift in a collision between particles with spherically symmetric potentials is obtained, using the method of Curtiss and Powers. In this expression the potential is not restricted to monotonic functions; the results apply to a potential with an attractive minimum. The classical limit and the first quantum correction, both developed earlier for monotonic potentials, are also re-derived so that they may be used with potentials possessing a minimum. These expressions are then used to develop series expressions for $Q^{(1)}$ and $Q^{(2)}$, the so-called cross sections for diffusion and viscosity, respectively. These expressions for $Q^{(1)}$ and $Q^{(2)}$ are used to obtain the classical limit and the quantum corrections to the transport collision integrals.

ABSTRACT (cont'd)

In the case of $Q^{(2)}$ the effect of statistics on collisions between like molecules is also considered. It is found that $Q^{(2)}$ is not modifed by statistics, at least through terms of order $h^4$.

THE THEORY OF ATOMIC COLLISIONS by Donald Kouri (supported by NASA and NSF).

Report No. WIS-TCI-112                              dated 30 July 1965

Will be published in three parts.

## ABSTRACT

The separation of the rotational degrees of freedom from the N particle Schrödinger equation is discussed and applied to the system $H^+ - H$. A symmetric definition of the Euler angles is employed thus facilitating the inclusion of the effects of the Pauli principle due to the identity of the protons. The solutions of the coupled partial differential equations which are obtained are expanded in terms of Born-Oppenheimer $H_2^+$ electronic wave functions and the resulting coupled equations investigated. A selection rule restricting the coupling to states of a single symmetry is derived and the asymptotic behavior of the coupled differential equations considered. Next a truncation scheme for treating the coupled equations is presented.

Use is then made of the formal scattering theory to obtain the asymptotic form of the desired wave function. This result is used to specify the arbitrary constants in the general solution of the Schrödinger equation. The resulting solution describes asymptotically an incoming plane wave and outgoing scattered spherical waves. The condition that this general solution vanish at the origin suffices to determine the scattering amplitudes, which in turn are shown to be related to the cross sections in a simple fashion.

ABSTRACT (cont'd)

Finally, the practical aspect of obtaining the numerical solutions of the coupled equations is treated. The problem of determining the phase shifts for elastic scattering is discussed. A new numerical method for evaluating phase shifts based on the fact that the phase and amplitude of the wave function are slowly varying functions is developed. A new relation for the absolute phase shift is obtained and shown to be useful in generalizing the W.K.B. method for obtaining phase shifts to any number of turning points. Then an analogous numerical scheme for coupled equations is developed based on the same concept of slowly varying phase and amplitude of the solutions of the coupled equation.

REMARKS ON THE CALCULATION OF VAN DER WAAL'S ENERGY by S. T. Epstein (supported by NASA).

Report No. WIS-TCI-113                                        dated 9 August 1965

Scheduled to be published in the 12/15/65 issue of J. Chem. Phys.

### ABSTRACT

We have looked for conditions under which the van der Waal's energy calculated by means of variationally determined polarizabilities according to the formula of Mavroyannis and Stephens, is an upper bound to the true energy. The conditions we find are quite restrictive.

A PERTURBATION THEORY OF ISOELECTRONIC MOLECULES: APPLICATION TO CO BASED ON $N_2$ by Tai Yup Chang and W. Byers Brown (supported by NASA).

Report No. WIS-TCI-114                                        dated 9 August 1965

Submitted for publication to Theoretica Chimica Acta.

### ABSTRACT

A perturbation theory of heteronuclear diatomic molecules based on isoelectronic homonuclear diatomic molecules is developed. The heteronuclear

## ABSTRACT (cont'd)

molecule is regarded as the isoelectronic homonuclear molecule perturbed by a transfer of charge from one nucleus to the other. The molecular energy, equilibrium internuclear distance, dissociation energy, and electric dipole moment are considered. The Hartree-Fock approximations for calculating the effect of one-electron perturbations are also discussed.

The theory is applied to the isoelectronic molecules CO and $N_2$. By making use of the uncoupled Hartree-Fock approximation, the first-order wave function in the perturbation series is determined by the variational method. The calculated molecular energy of CO is too low and the dipole moment is too large in magnitude. However the calculated polarity is in agreement with the results of recent Hartree-Fock calculations at the equilibrium distance.

A DOUBLE PERTURBATION TREATMENT OF THE GROUND STATE OF THE HYDROGEN MOLECULE by Bowen Liu, W. D. Lyon and W. Byers Brown (supported by NASA and NSF).

Report No. WIS-TCI-115                                    dated 11 August 1965

Scheduled to be published in the 1/15/66 issue of J. Chem. Phys.

### ABSTRACT

The ground state of the hydrogen molecule is treated by a double perturbation theory through second order. The unperturbed system is defined mathematically by the unperturbed spatial wave function, which has the form $\exp[-s(r_{a1}+r_{b1}+r_{a2}+r_{b2})]$ where $s$ is an energy-optimized scale parameter. The perturbations are (a) one-electron terms due to the simple form chosen for the zeroth order wave function, and (b) the two-electron repulsion potential. The first order wave function for (a) is known analytically, and that for (b) is obtained approximately from the Hylleraas

ABSTRACT (cont'd)

variational principle using a James-Coolidge type trial function.

The energy through second order gives an equilibrium distance within one per cent of that obtained by Kolos and Roothaan and a dissociation energy of 4.9884 eV, five per cent larger than their value of 4.7467 eV. The wave function through first order gives expectation values for one-electron operators in good agreement with accurate calculations, but is poor when the electrons are close together.

THE 1/Z PERTURBATION THEORY OF THE HOOKE'S LAW MODEL FOR THE TWO-ELECTRON ATOM by Ronald J. White and W. Byers Brown (supported by NASA).

Report No. WIS-TCI-116                                   dated 29 August 1965

Will be submitted for publication to J. Math. Phys.

ABSTRACT

The aim of this paper is to contribute to the study of the first-order perturbation equation for the two-electron atom, which has not yet been solved. The corresponding equation for the ground state of a model atom is solved analytically. In the model the Coulomb attraction of the nucleus is replaced by a Hooke's law attraction (harmonic oscillator potential) while the interaction of the electrons remains coulombic. The first-order equation for the Hartree-Fock approximation is also solved analytically. The perturbation energies for the exact and Hartree-Fock treatments are obtained through third order.

THE GROUND STATE ENERGY OF A MOLECULE IN THE ADIABATIC APPROXIMATION by S. T. Epstein (supported by NASA).

Report No. WIS-TCI-118                                   dated 25 August 1965

Scheduled to be published in the 1/15/66 issue of J. Chem. Phys.

CONSTRAINED VARIATION METHOD IN MOLECULAR QUANTUM MECHANICS. COMPARISON OF DIFFERENT APPROACHES by D. P. Chong and Yecheskel Rasiel (supported by NASA).

Report No. WIS-TCI-119                                    dated 26 August 1965

Submitted for publication to J. Chem. Phys.

### ABSTRACT

Numerical results are presented for the lithium hydride molecule, obtained by different techniques of the constrained variation method. The constrained wave function, the degree to which the constraint is satisfied, and the sacrifice in energy are compared. The constraint operator used was the electronic dipole moment in one case and the total Hellmann-Feynman force in another. In both cases, the parametrization procedure in the direct solution approach (Method IB) was found to be superior.

IMPROVEMENT OF UNCOUPLED HARTREE-FOCK EXPECTATION VALUES FOR PHYSICAL PROPERTIES by Debbie Fu-tai Tuan, Saul T. Epstein and Joseph O. Hirschfelder (supported by NASA).

Report No. WIS-TCI-121                                    dated 4 September 1965

Scheduled to be published in the 1/15/66 issue of J. Chem. Phys.

### ABSTRACT

It is shown that if one uses the uncoupled Hartree-Fock method as a zero-order approximation for calculating atomic and molecular second-order properties (either static or dynamic), then the first order corrections to this approximation are determined solely by quantities already available from the zero-order calculations. No new equations need be solved.

THE CUSP CONDITIONS FOR MOLECULAR WAVE FUNCTIONS by Russell T. Pack and Joseph O. Hirschfelder (supported by NASA and NSF).

Report No. WIS-TCI-123                                    dated 5 November 1965

Will be submitted for publication to J. Chem. Phys. in revised form.

## ABSTRACT

The cusp conditions are derived which describe the behavior of the wave function at the singularities of the Coulomb potential corresponding to the coalescence of two or more particles. In this derivation, the wave function is not spherically averaged; the fixed-nuclei approximation is not required; and the wave function may have nodes at the singular points. In addition to the general treatment, the cusp conditions for diatomic molecules are discussed in three different coordinate systems.

LONG RANGE (RETARDED) INTERMOLECULAR FORCES by William J. Meath and Joseph O. Hirschfelder (supported by NASA and NRC-Canada).

Report No. WIS-TCI-124                                    dated 21 September 1965

Scheduled to be published in the 2/15/66 issue of J. Chem. Phys.

## ABSTRACT

The Casimir and Polder retarded dipole-dipole energy of interaction between two ground state (non-degenerate) atoms is expressed in terms of Sine and Cosine integrals. This result should be accurate for all inter-atomic separations of R . In the range of moderately large separations (discussed in the preceding paper) where the charge distributions do not overlap and where R is small compared to $\lambda_0 = (\alpha \Delta E)^{-1}$ , the Casimir and Polder results can be expanded in the form

$$E_{int} = R^{-6} C_6 + \alpha^2 R^{-4} W_4 + \alpha^3 R^{-3} A + \alpha^4 R^{-2} B + \dots$$

This expansion is only accurate for $R/\lambda_0 < 0.6$. Here $\alpha$ is the fine structure constant. The $R^{-6} C_6$ term is the usual London dispersion energy. The $\alpha^2 R^{-4} W_4$ term was obtained in the preceding paper by taking the expectation value of the Breit-Pauli Hamiltonian using the wave function for the two-atom system corrected for the classical electrostatic dipole-

ABSTRACT (cont'd)

dipole interactions. Thus, at least in the dipole-dipole approximation, the
Breit-Pauli Hamiltonian gives the energy of interaction accurate through
$0(\alpha^2)$. For large values of $R/\lambda_o$, the interaction energy is expanded
in the series

$$E_{int} = \alpha^{-1} R^{-7} D + \alpha^{-3} R^{-9} F + \alpha^{-5} R^{-11} G + \ldots$$

This large R expansion is only accurate for $R/\lambda_o > 5.0$.

ONE- AND TWO-CENTER EXPANSIONS OF THE BREIT-PAULI HAMILTONIAN by Peter R.
Fontana and William J. Meath (supported by NASA).

Report No. WIS-TCI-125                              dated 7 December 1965

ABSTRACT

The orbit-orbit, spin-spin and spin-orbit Hamiltonians of the Breit-
Pauli approximation are expressed in terms of irreducible tensors. One-
and two-center expansions are given in a form in which the coordinate
variables of the interacting particles are separated. In the one-center
expansions of the orbit-orbit and spin-orbit Hamiltonians the use of the
gradient formula reduces some of the infinite sums to finite ones. Two
center expansions are discussed in detail for the case of non-overlapping
charge distributions. The angular parts of the matrix elements of these
Hamiltonians are evaluated for product wave functions.

INTRINSIC INTRACTABILITY IN AB INITIO QUANTUM MECHANICAL CALCULATIONS ON
COMPLICATED SYSTEMS by Thomas H. Walnut (this work was not supported by
any of our contracts or grants).

Report No. WIS-TCI-127                              dated 15 July 1965

## ABSTRACT

The hypothesis is made that ab initio quantum mechanical calculations of most properties of complicated molecules and solids are intrinsically intractable. It is shown that such a hypothesis is reasonable. The consequences of the hypothesis are examined. The concept of an ensemble of systems which differ by very small changes in their Hamiltonians is introduced. It is found that under these conditions properties would be unpredictable unless the system behaved as an ordinary member of the ensemble. The assumption that naturally occurring complicated systems behave as ordinary members of an ensemble of similar systems is found to be consistent with observation. The ensemble introduces statistical techniques in solving complicated problems and consequently results of such calculations should be subject to fluctuations. In this way random phase properties arise naturally in complicated systems.

THE SUDDEN APPROXIMATION APPLIED TO MOLECULAR PROBLEMS. I. NON-REACTIVE COLLISIONS by J. L. J. Rosenfeld (supported by NASA and Advanced Research Project Agency-Brown).

Report No. WIS-TCI-128                              dated 27 September 1965

Will be submitted for publication in revised form.

## ABSTRACT

The sudden approximation for transition probabilities is derived using an evolution operator formalism. The assumptions required are explicitly stated and their validity and applicability are discussed in relation to energy transfer during collisions between molecules and atoms. It is shown that sufficient conditions ensuring the validity of the sudden approximation are (1) that a classical description be adequate to describe the relative motion of the molecules or atoms, and (2) that the energy levels of the states mainly involved in the process be such that the product of their energy difference and the collision time be small compared to $\hbar$ .

THE APPLICATION OF PERTURBATION THEORY TOWARD THE DETERMINATION OF MOLECULAR ENERGIES AND PROPERTIES by Robert L. Matcha (supported by NASA).

Report No. WIS-TCI-129                                          dated 15 October 1965

Will not be published in this form.

## ABSTRACT

The ground state energy of the hydrogen molecule is accurately determined with the aid of Rayleigh Schroedinger perturbation theory, treating the electronic interaction as a perturbation to the remaining Hamiltonian. Techniques are developed for evaluating integrals containing zeroth order $H_2^+$ wave functions. A generalized Hylleraas variational method is used to determine wave functions beyond zeroth order.

The perturbation energy through fifth order at the equilibrium separation is found to be comparable in accuracy to the most accurate variational calculations.

A PERTURBATION THEORY OF ISOELECTRIC MOLECULES:  CONVERGENCE OF SERIES FOR ONE DIMENSIONAL DELTA POTENTIAL MODEL by Pearl S. C. Wang and W. Byers Brown (supported by NASA).

Report No. WIS-TCI-130                                          dated 17 November 1965

Will be submitted for publication to Theoretica Chimica Acta.

## ABSTRACT

The perturbation theory of heteronuclear molecules based on isoelectronic homonuclear molecules developed by Chang and Byers Brown is applied to the delta potential model. The radii of convergence of the series expansions for the energy and dipole moment are obtained. The errors in the perturbation treatment due to neglect of higher order terms are calculated. The results tend to support the application of this theory to the $CO-N_2$ problem.

THE QUANTUM MECHANICAL KINETIC THEORY OF LOADED SPHERES by John J. Mueller (supported by NASA and NSF).

Report No. WIS-TCI-131                               dated 25 October 1965

Will not be published in this form.

## ABSTRACT

The transport coefficients of a gas of loaded spheres, that is, spheres in which the center of mass does not coincide with the geometrical center are considered. The amount by which the center of mass is displaced from the center of the sphere is denoted by $\delta$ and the diameter of the sphere is $\sigma$. The scattering amplitude and cross section are found as power series in $\delta/\sigma$; the coefficients of the zero, first, and second power of $\delta/\sigma$ are obtained. Using these results, the quantum mechanical expressions for the relaxation time, coefficient of shear viscosity, and coefficient of thermal conductivity are also obtained explicitly to second order in $\delta/\sigma$. These quantities are then evaluated, numerically, in the limit that Planck's constant approaches zero. The results are found to agree with results obtained by purely classical methods.

PATH-INTEGRALS IN DYNAMICS by A. M. Arthurs (supported by NASA and U. S. Army).

Report No. WIS-TCI-132                               dated 1 November 1965

Submitted for publication to J. Math. Phys. in revised form.

## ABSTRACT

The Lagrangian formulation of quantum dynamics in terms of path-integrals due to Feynman describes systems for which the Hamiltonian is classical in form and quantization is carried out in terms of commutators rather than anticommutators. The difficulty with the Feynman method is the actual evaluation of the path-integral itself. We give an explicit

ABSTRACT (cont'd)

evaluation for classical wave motion in one dimension. This requires an

extension of the Feynman method which was introduced by Tobocman and

studied in detail by Davies.

We also discuss the work of Corson on the question of a unified

formulation of dynamics.


NUMERICAL EVALUATION OF BARRIER PENETRATION AND RESONANCE EFFECTS ON PHASE
SHIFTS by R. B. Bernstein, C. F. Curtiss, S. Imam-Rahajoe, and H. T. Wood
(supported by NASA).

Report No. WIS-TCI-133                            dated 27 December 1965

To be submitted for publication in the J. Chem. Phys.

## ABSTRACT

Quantum mechanical calculations, based on the Lennard-Jones (12,6)

potential, are presented showing the dependence of the reduced phase shift,

$\eta^*$, on the quantum parameter, $\Lambda^*$, for a fixed reduced effective

potential and various reduced energies, $E^*$. The observed oscillatory

behavior of $\eta^*(\Lambda^*)$ is due primarily to the inclusion of the physically

unimportant contribution of $M\pi$ to the phase shift, where $M$ is the

number of quasi-bound (virtual) states of energy less than $E^*$. A

modified reduced phase shift, $\tilde{\eta}^*$, defined by excluding this contribution,

displays only the sharp inflections associated with barrier penetration

under esonance conditions. Except for the resonance contribution, the

phase shifts may be accurately reproduced by a second-order JWKB procedure.

This method also accurately predicts the resonant energies (i.e. the energies

of the quasi-bound states). The first-order JWKB treatment of the barrier

penetration problem by Ford, Hill, Wakano, and Wheeler suffices for the

purpose of estimating the level widths and lifetimes of the virtual states

as well as the main features of the resonant phase shifts, but does not

accurately reproduce the quantal calculations.

CALCULATED ELASTIC SCATTERING CROSS SECTIONS FOR THE $H^+$ - He SYSTEM by
Gunter G. Weber, Nahida H. Gordon and R. B. Bernstein (supported by NASA).

Report No. WIS-TCI-134                    dated 3 November 1965

Submitted for publication to J. Chem. Phys.

ABSTRACT

The ab initio computations by Michels and Harris, and Pyerimhoff, of
the ground $(^1\Sigma^+)$ state of $HeH^+$ provide a reliable interaction potential
$V(r)$ to serve as a basis for prediction of proton-helium elastic scattering.
This report summarizes calculations of total elastic cross sections, $Q(E)$,
for low collision energies (E in the range 0.3 - 200 eV) where Q is
sensitive primarily to the attractive part of $V(r)$. Superimposed upon
the monotonic $E^{-\frac{1}{3}}$ dependence (arising from the long-range $r^{-4}$ "tail"
of the potential) are a number of broad extrema in $Q(E)$, characteristic
of a potential well with the capacity for several ($\geq 7$) bound (vibrational)
states.

APPLICABILITY OF PERTURBATION THEORY TO MOLECULAR PROBLEMS by Joseph O.
Hirschfelder (supported by NASA).

Report No. WIS-TCI-135                    dated 11 November 1965

Proc. of Advanced Seminar on Perturbation Theory and Its Application in
Quantum Mechanics, John Wiley and Sons, Inc., 1966.

ABSTRACT

This paper is a general survey of the ways in which low order per-
turbation theory is used in quantum mechanics to determine the energy and
other properties of molecules. The various types of mathematical problems
encountered are discussed.

BIPOLAR ANGLE AVERAGES AND TWO-CENTER, TWO-PARTICLE INTEGRALS INVOLVING $r_{12}$
by M. B. Milleur, M. Twerdochlib, and J. O. Hirschfelder (supported by NASA).

Report No. WIS-TCI-136                    dated 30 November 1965

Submitted for publication to J. Chem. Phys.

## ABSTRACT

The bipolar angle average of a two-center, two-particle function $f(r_{a1}, r_{b2}, r_{12};R)$ is $\langle f \rangle = (4\pi)^{-2} \iint f \, d\omega_{a1} \, d\omega_{b2}$. A bipolar angle average weight function $L_o$ is derived from geometrical considerations such that $\langle f \rangle = \int_{r_{12}(min)}^{r_{12}(max)} f L_o \, dr_{12}$. The $L_o$ is independent of $f$ and has a different, although simple, functional form in each of 42 regions of $r_{a1}$-$r_{b2}$-$r_{12}$ space. However, the $\langle f \rangle$ have different functional forms in only four regions of $r_{a1}$-$r_{b2}$ space. The expressions which we derive for the bipolar angle average are surprisingly simple and general, requiring only the evaluation of integrals of the form $\int f \, r_{12} dr_{12}$ and $\int f \, r_{12}^2 dr_{12}$. The bipolar angle averages are very useful in the evaluation of two-center, two-particle integrals. Many of our relations are greatly simplified by the use of homogeneous coordinates.

EXISTENCE OF TWO PHASES IN ONE-DIMENSIONAL CLASSICAL FLUIDS by F. C. Andrews and John M. Benson (supported by NASA and NSF).

Report No. WIS-TCI-140                                    dated 30 November 1965

Accepted for publication in Physics Letters.


ON THE THEORY OF DROPLET FORMATION IN ONE-DIMENSIONAL FLUIDS by F. C. Andrews (supported by NSF).

Report No. WIS-TCI-141                                    dated 2 December 1965

Accepted for publication in Physics Letters.

APPROXIMATE PERTURBATION TREATMENT OF $H_2^+$ by William D. Lyon, William A. Sanders and Joseph O. Hirschfelder (supported by NASA).

Report No. WIS-TCI-142                                    dated 13 December 1965

Submitted for publication to J. Chem. Phys.

## ABSTRACT

A procedure for approximating a correct perturbation of two interacting atoms in the region of overlap was used to calculate the energy of $H_2^+$. As a result of symmetry considerations, the results were not promising.

Additional Publications During the Period July 1, 1965 - December 31, 1965

"Guillemin-Zener Energy of $H_2^+$" by Sungwoon Kim, Tai Yup Chang, and J. O. Hirschfelder (WIS-TCI-40A), J. Chem. Phys., 43, 1092 (1965).

"On the Solution of the BBGKY Equation for a Dense Classical Gas" by F. C. Andrews (WIS-TCI-70), J. Math. Phys., 6, 1496 (1965).

"Determination and Assessment of Morse Potential Functions for Some Non-polar Gases" by D. D. Konowalow and S. Carra (WIS-TCI-74), Phys. of Fluids, 8, 1585 (1965).

"Phase Shifts and the Quantum Mechanical Hamilton-Jacobi Equation" by Donald J. Kouri and C. F. Curtiss (WIS-TCI-81), J. Chem. Phys., 43, 1919 (1965).

"Dipole Matrix Elements for Helium in the First-Order Sheilding Approximation" by Kenneth M. Sando and Saul T. Epstein (WIS-TCI-82), J. Chem. Phys., 43, 1620 (1965).

"Perturbation Treatment of the Ground State of $H_2^+$" by William D. Lyon, Robert L. Matcha, William A. Sanders, William J. Meath and Joseph O. Hirschfelder (WIS-TCI-85), J. Chem. Phys., 43, 1095 (1965).

"Perturbation Treatment of the Ground State of $HeH^{++}$" by Robert L. Matcha, William D. Lyon and Joseph O. Hirschfelder (WIS-TCI-87), J. Chem. Phys., 43, 1101 (1965).

"Internal Energy of Reaction Products by Velocity Analysis. II. Scattered $KBr^*$ from the Crossed Molecular Beam Reaction $K + Br_2$" by Arthur Grosser and R. B. Bernstein (WIS-TCI-88X), J. Chem. Phys., 43, 1140 (1965).

"Long-Range Interaction of Two 1s-Hydrogen Atoms Expressed in Terms of Natural Spin-Orbitals" by J. O. Hirschfelder and P. O. Lowdin (WIS-TCI-92), Mole. Phys., 9, 491 (1965).

"Quantum-Mechanical Boltzmann Equation" by David K. Hoffman, John J. Mueller, and C. F. Curtiss (WIS-TCI-95), J. Chem. Phys., 43, 2878 (1965).

"Direct Calculation of Contributions to the Second-Order Energy of Helium" by Bowen Liu, William J. Meath and J. O. Hirschfelder (WIS-TCI-96), J. Chem. Phys., 43, No. 10 (Part 1), 3756 (1965).

"Discussion Following Pauncz's Paper" by D. P. Chong, J. Chem. Phys., 43, No. 10 (Part 2), S73 (1965).

"Determination of Intermolecular Forces" by J. O. Hirschfelder, J. Chem. Phys., 43, No. 10 (Part 2), S199 (1965).

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